

Dichlorocarbene Formation from Thallium (I) Butanethiolate and Chloroform

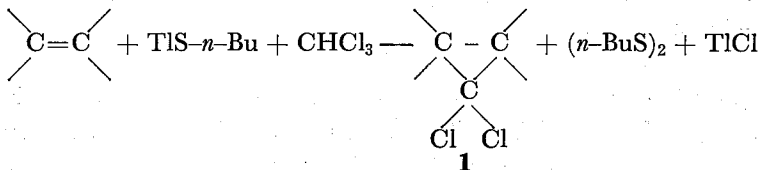
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The reactions of cyclohexene and α -methylstyrene with thallium(I) butanethiolate (TIS-*n*-Bu) in chloroform at a refluxing temperature for 3 h gave the corresponding *gem*-dichlorocyclopropane derivatives in 11% and 22% yield respectively. Other thiolates of thallium(I) such as TISEt, TIS-*t*-Bu, and TISPh, and other metal butanethiolates such as Pb(S-*n*-Bu)₂ and NaS-*n*-Bu showed lower reactivity than TIS-*n*-Bu for the generation of dichlorocarbene.

In contrast to the numerous works on the chemical reactivities of thallium(I) alkoxides and phenoxides,¹⁾ the studies on thallium(I) thiolate have so far been limited to only one case.²⁾ We now wish to report the first example of dichlorocarbene formation from thallium(I) alkanethiolate and chloroform.³⁾ The generation of dihalocarbenes from thallium(I) ethoxide and haloforms is known.⁴⁾

When a mixture of thallium(I) butanethiolate, chloroform, and cyclohexene or α -methylstyrene was heated at a refluxing temperature for 3 h, the corresponding *gem*-dichlorocyclopropane derivative (**1**) was obtained in 11% or 22% yield respectively, together with 35–41% yield of dibutyl disulfide and small amounts of high-boiling substances. It was also confirmed that nearly the same amounts of the di-



sulfide and high-boiling substances were formed under similar conditions without the addition of olefin. The disulfide must be formed by the oxidation of the thiol formed first, as the catalytic effect of thallium(I) salt for the oxidation of the thiol is known.⁵⁾ Thallium(I) salt was recovered mainly as the chloride. The reaction proceeded even at 20–30°C, though it was sluggish (*i.e.*, 10% yield of **1** from cyclohexene for 24 h). When the reaction of α -methylstyrene was carried out in the presence of equimolar amounts of crown-ether (dicyclohexyl-18-crown-6) to thallium (I) salt, the yield of **1** was decreased from 22% to 13% despite of the nearly homogeneous reaction, the amount of high-boiling substances being almost unchanged. This may suggest that un-ionized thallium(I) butanethiolate itself acts as a base to

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generate dichlorocarbene. The use of other thiolates of thallium(I) such as TlSEt, TlS-*t*-Bu, and TlSPh did not improve the yield of **1**. The reaction with lead(II) butanethiolate gave only 3% yield of **1** from cyclohexene at a refluxing temperature for 3 h.

Alkali alkoxides are known to be a good reagent for dihalocarbene generation. Sodium butanethiolate, however, was revealed to be ineffective for the formation of **1**, only 2% and 7% yield of **1** being obtained from cyclohexene and α -methylstyrene respectively at a refluxing temperature for 3 h. Instead, side reactions giving such high-boiling substances as above occurred favorably, the amount of which was nearly three times as much as that in the case of thallium(I) butanethiolate. Some of these compounds were revealed to be $\text{CH}(\text{S}-n\text{-Bu})_3$, $\text{CH}_2(\text{S}-n\text{-Bu})_2$, and $\text{Cl}(\text{S}-n\text{-Bu})\text{C}=\text{C}(\text{S}-n\text{-Bu})_2$. Substitution of chlorine of chloroform by ethanethiolate has been long known.⁶⁾

EXPERIMENTAL

Materials. The Tl(I) or Pb(II) butanethiolate was prepared by the slow addition of an ethanol (5 ml) solution of butanethiol (20 mmol) to the corresponding metal acetate (5–10 mmol) in ethanol (5–10 ml) at room temperature and by the filtration of the yellow or white air-stable solid after 1–3 h's stirring respectively: TlS-*n*-Bu, mp 80–85°C (lit,⁷⁾ mp 84–90°C); Pb(S-*n*-Bu)₂, mp 62–63°C (Found: C, 24.41; H, 4.97%. Calcd for C₈H₁₈S₂Pb: C, 24.92; H, 4.71%). TlSEt (mp 140–145°C) and TlSPh (mp 255–260°C; lit,⁷⁾ mp 258–260°C) were similarly prepared as above, while it was necessary to make the reaction mixture alkaline by the addition of aqueous NaOH for the preparation of TlS-*t*-Bu (mp 170–175°C; lit,⁸⁾ mp 170–175°C). In all cases the yields were almost quantitative. NaS-*n*-Bu was prepared from Na and butanethiol. Authentic samples of **1** were synthesized by the reaction of olefins with KO-*t*-Bu and chloroform.⁹⁾

Reaction of TlS-*n*-Bu with Cyclohexene in Chloroform. A freshly prepared yellowish orange TlS-*n*-Bu (2.20 g, 7.5 mmol) was added to a mixture of cyclohexene (10 ml) and chloroform (15 ml) at 35°C. An exothermic reaction occurred immediately, and the color of the mixture turned to red-brown and then to pale yellow. After the resulting heterogeneous mixture was heated under reflux (65°C) for 3 h, the precipitate [1.22 g, a mixture of TlCl (94%) and TlS-*n*-Bu (6%) by IR spectrum and elemental analysis] was filtered off. The GLC analysis of the filtrate revealed the presence of 1, 1-dichloronorcarane (0.83 mmol, 11% yield) and dibutyl disulfide (1.54 mmol, 41% yield) together with small amounts of high-boiling substances, some of which being revealed to be the same as those obtained in the reaction with NaS-*n*-Bu (see below) [iodobenzene as an internal standard; Shimadzu 4BMPF apparatus; Apiezon-L(30%)-Celite (1 m) column, N₂ as carrier gas]. In the case of α -methylstyrene, ethylbenzoate was used as an internal standard on EGSS-X(15%)-Chromosorb-W (1 m or 3 m) column. In both cases **1** was isolated by distillation from the combined distillates of several reactions, and was confirmed by comparison with an authentic sample in NMR and mass spectra, and the retention time in GLC

on several different columns.

Reaction of NaS-*n*-Bu with Chloroform. A mixture of NaS-*n*-Bu (0.88 g, 7.5 mmol) and chloroform (20 ml) was stirred for 3 h under reflux. After being cooled down, water was added and organic layer was separated. The GLC analysis of the residue after evaporation of chloroform revealed the presence of dibutyl disulfide (10% yield) and high-boiling substances. Distillation of the combined residue of two runs afforded 0.35 g of the distillate (bp 55–78°C/2 Torr) which was revealed to contain CH(S-*n*-Bu)₃, CH₂(S-*n*-Bu)₂, CHCl(S-*n*-Bu)₂, Cl(S-*n*-Bu)C=C(S-*n*-Bu)₂ (ca. 1.5: 1: 1.5: 3 by NMR) and some small amounts of unidentified compounds by NMR and mass spectra: the last compound, *m/e* 326 (M⁺), 328 (M⁺+2), 269 (M⁺-Bu), 271 (M⁺+2-Bu).

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